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(54) Title: ELECTROREFINING PROCESS FOR SEPARATING METALS

(57) Abstract: The invention comprises an electrorefining process for separating a metal from a composition including the said metal, the method comprising forming an electrorefining cell having an anode, a cathode and an electrolyte, wherein the anode comprises the metal and the electrolyte comprises a substance which is liquid at its operating temperature and at this temperature is comprises wholly or largely of ionic species, and applying a sufficient potential difference between the anode and the cathode to cause the metal to transfer from the anode to the cathode and to be deposited thereon, wherein gap between the anode and the cathode is minimised, the electrolyte is circulated at high velocity through the cell, and the available surface area of the cathode is maximised by providing the metal in a form which has a large surface area per unit volume. In preferred embodiments, either the anode is in the form of a basket, and the metal composition is provided in a finely divided form within the said basket or the metal composition is provided in the form of a long, thin rod which itself forms the anode. Preferably, the composition including the metal comprises spent nuclear fuel, and the electrolyte comprises an ionic liquid.

ELECTROREFINING PROCESS FOR SEPARATING METALS

FIELD OF THE INVENTION

5   This invention relates to processes for the separation of metals from compositions containing metals. The invention includes processes for the treatment of spent nuclear fuel forming part of a process for reprocessing, conditioning and/or partitioning nuclear fuels. Reference will be made hereinafter mainly to nuclear fuels but it should be understood that the invention is not restricted to any particular type

10   of material and has application outside the nuclear industry. The processes involve the purification of a substance which is liquid at its operating temperature and at this temperature is comprised wholly or largely of ionic species. Such substances generally fall within one of two main classes, ionic liquids and molten salts. Ionic liquids typically have a melting point of less than 100°C and usually contain an

15   organic cation, whereas molten salts are generally totally inorganic and most commonly have a melting point of at least several hundred degrees Centigrade. Molten salts typically comprise eutectic mixtures, the melting points of which can be significantly depressed from those of the individual components.

20   ## BACKGROUND TO THE INVENTION

In the metals recovery and refining industry generally, the type of metal recoverable from a solvent is dependent upon the size of the electrochemical window of the solvent in which the metal is dissolved, and from which purification and recovery is

25   taking place. In aqueous solutions, this is governed by the electrochemical window of water or supporting electrolyte. This limits the recovery, purification and electroplating of metals on to surfaces from aqueous solution to those metals whose electrode reduction potentials are more positive than the cathodic limit of the aqueous solution. In acidic aqueous solution, metal ions would not be recoverable

30   where their electrode reduction potentials are more negative than that of the H_3O^+ ion. Recovery of metals with electrode reduction potentials more negative than

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H_3O^+, means that non-aqueous (aprotic) solvents are required. There are a number of aprotic solvents which are used. These are often molten salts and, for instance, aluminium is industrially purified electrochemically by electrolysis of Al_2O_3 dissolved in molten cryolite Na_3AlF_6. Other aprotic media include the organic

5 solvents, such as acetonitrile, benzene and toluene.

Molten salts are often used as media in the nuclear industry. Such salts may be eutectic mixtures of salts and comprise chloride salts such as sodium or lithium chloride. These molten salts are typically liquid only at high temperatures.

10 Alternatively, as previously noted, ionic liquids may be employed; the said term may refer to a salt, a mixture of salts, a mixture of components which produce a salt or salts which melts below or just above room temperature. (As used herein, the term "salt" means an entity comprising entirely of cationic and anionic species). The liquids are known as "ionic liquids" although this term is sometimes used for salts

15 which melt at relatively high temperatures. In this specification, the term "ionic liquid" essentially refers to a salt which melts at a temperature of up to 100°C. Ionic liquids free of molecular solvents were first disclosed by Hurley and Wier in a series of US patents (2446331, 2446349, 2446350).

20 Common features of ionic liquids include a zero vapour pressure at room temperature, a high solvation capacity and a large liquid range (for instance, of the order of 300°C). Known ionic liquids include aluminium(III) chloride in combination with an imidazolium halide, a pyridinium halide or a phosphonium halide. Examples include 1-ethyl-3-methylimidazolium chloride, N-butylpyridinium

25 chloride and tetrabutylphosphonium chloride. An example of a known ionic liquid system is a mixture of 1-ethyl-3-methylimidazolium chloride and aluminium (III) chloride.

Internationally there are two well developed molten salts processes for the

30 reprocessing/waste conditioning of irradiated nuclear fuel. A process developed by the Dimitrovgrad SSC - RIAR process uses high temperature (1000K) eutectic

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molten salt mixtures as solvents for the fuel and also as electrolyte systems. In this Russian system the solvent is an eutectic mixture of NaCl/KCl or CsCl/KCl. The process uses chemical oxidants (chlorine and oxygen gases) to react with powdered UO_2 fuel to form higher oxidation state compounds such as UO_2Cl_2 which are

5   soluble in the molten salt. At the cathode the uranium compounds are reduced to UO_2, which forms a dendritic deposit. However, after a period of use the molten salt becomes loaded with fission products which not only begin to affect the quality of the product, but also result in too much heat generation within the salt. These fission products are commonly, but not exclusively, highly active lanthanide or actinide

10   elements which need to be isolated in a suitable form for immobilisation as a waste.

In the process developed by Argonne National Laboratory (ANL) in the USA, molten LiCl/KCl eutectic mixtures are generally used, rather than systems containing sodium or caesium salts, and a high temperature (773K) is again employed. The process

15   treats the spent nuclear fuel by flowing a current to oxidise a uranium anode and form uranium ions in the molten salt electrolyte. At the cathode the uranium is reduced and deposited as uranium metal. The ANL process is, unfortunately, a batch process, since the uranium is collected in a receptacle at the bottom of the apparatus, requiring that the process is interrupted in order that the receptacle may be withdrawn and the

20   product recovered. In addition, the operation of the process is mechanically intense, involving the use of rotating anodes which are designed to scrape the product off the cathodes; difficulties are encountered on occasions due to the seizure of this mechanism.

25   Co-pending patent application PCT/GB99/00246 discloses a method for reprocessing spent nuclear fuel which comprises dissolving the spent fuel or constituent parts of the spent fuel in an ionic liquid to substantially separate fissile material from other components of irradiated fuel. Also disclosed is the subsequent treatment of the resulting ionic liquor, either by solvent extraction or electrochemical treatment to

30   recover the dissolved uranium and plutonium. However, these processes for the clean up of the ionic liquid are disadvantageous from an economic point of view.

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Furthermore, whilst the methods described in PCT/GB99/00246 are technically suitable for general use and, in particular, for use in nuclear fuel reprocessing, it has previously been thought that an electrorefining process, which avoids the need for an initial chemical dissolution step, requires the use of a high temperature molten salt

5 electrolyte. If fuel is chemically oxidatively dissolved, there is less control over the species which are dissolved during this step. All those species which will be oxidised by the oxidising agent added will enter into the solution. Because the oxidising agents and conditions are aggressive, most species will dissolve except for species such as the noble metals.

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Co-pending patent application PCT/GB00/03194 discloses a method for separating a metal from a composition including the said metal, the method comprising forming an electrolytic cell having an anode, a cathode and an electrolyte, wherein the anode comprises a composition including the metal and the electrolyte comprises an ionic

15 liquid, and applying a sufficient potential difference between the anode and the cathode to cause the metal to transfer from the anode to the cathode and to be deposited thereon.

However, when this method is applied to a composition which comprises a metal or

20 metal compound comprising a uranium or a transuranic element, problems of criticality may arise, since ionic liquids serve as moderators in such systems. In such circumstances, the difficulties may be obviated by placing a limit on the allowable diameter of the electrochemical cell. The present inventors have found that particular advantages may be achieved by increasing the surface area per unit volume of the

25 anode and cathode and reducing the electrode separation, thereby maximising the cell current. In addition, it is beneficial to provide high electrolyte velocities, which result in a scouring action, helping to remove dendritic growth on the cathode, and also provide turbulent flow, thus reducing the boundary layer and subsequently increasing the mass transfer coefficient. The advantages initially observed with

30 uranium and transuranic elements are also applicable in the case of a wide range of other metals and metal compositions, and the process of the present invention has

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been found to be equally advantageous when using electrolytes which comprise molten salts, rather then ionic liquids.

STATEMENTS OF INVENTION

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Thus, according to the present invention there is provided an electrorefining process for separating a metal from a composition including the said metal, the method comprising forming an electrorefining cell having an anode, a cathode and an electrolyte, wherein the anode comprises the metal and the electrolyte comprises a

10   substance which is liquid at its operating temperature and at this temperature is comprised wholly or largely of ionic species, and applying a sufficient potential difference between the anode and the cathode to cause the metal to transfer from the anode to the cathode and to be deposited thereon, wherein the gap between the anode and the cathode is minimised, the electrolyte is circulated at high velocity through the

15   cell, and the available surface area of the cathode is maximised by providing the metal in a form which has a large surface area per unit volume.

The cell is designed such that the anode-cathode gap is minimised and the available surface area of the cathode is maximised, such that the mass transfer coefficient is

20   increased, leading to maximisation of the rate of operation. The returned electrolyte is such as to create turbulent flow which further increases the rate of mass transfer as well as facilitating removal of uranium from the cathode. This again increases the rate of the process and prevents electrical shorting between anode and cathode, which could result from growing metallic dendrites.

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The provision of the metal in a form which exhibits a large surface area per unit volume facilitates increased efficiency of the electrorefining process and enables the cell to be simply constructed, thereby leading to lower costs.

30   Once electrotransport is underway, the electrolyte is pumped at high velocity through the cell and, in particular, against the internal cathode surface; this reduces the

boundary layer, thereby facilitating increased rates of electrotransportation as well as sweeping the electrodeposit from the surface of the cathode. The boundary layer is the layer wherein the ion transport is subject to diffusion control, and its build-up should therefore be kept to a minimum in order to ensure the highest rates of

5 transport between the two electrodes. Since the exterior surface of the cathode may also be subject to electrodeposition, pumping against this surface is also necessary. In the alternative, however, the external surface may be coated with an insulating layer in order to avoid this phenomenon.

10 Desirably, the inter-electrode gap between the anode and the cathode should be in the range of from 1 mm to 30 mm. The optimum range for the electrolyte velocity is from 0.6 m/sec to 25 m/sec. The combination of these parameters is designed to maintain a turbulent flow regime in the cell. Ideally, the fluid flow and electrolyte parameter combination should lead to a Reynolds Number of greater than 2000, and

15 preferably in the region of 3000.

The material which comprises the electrolyte, comprising a substance which is liquid at its operating temperature and at this temperature is comprised wholly or largely of ionic species, typically comprises a molten salt or an ionic liquid.

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In a first embodiment of the invention, the anode is in the form of a basket, and the metal composition is provided in a divided form within the said basket.

In a second embodiment of the invention, the metal composition is provided in the

25 form of a long, thin rod which itself forms the anode.

Typically the composition including the metal comprises spent nuclear fuel in the form a metal fuel assembly of fuel pins. These assemblies are firstly dismantled to single pins for feeding to an electrorefiner cell. The first embodiment of the

30 invention then envisages cropping of the said pins into small sections; this may be conveniently carried out by means of a single pin cropping machine. The cropped

sections of fuel, which should be as small as possible in order to allow the electrolyte to act on the composition, are then loaded into the anode basket. In practice, a fuel pin is held in a suitable position and incrementally moved forward in order to ensure that the cropped sections are of suitably small dimensions.

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Alternatively, according to the second embodiment of the invention, a single fuel pin acts as the anode. Prior to insertion into the electrorefining cell, the cladding of the fuel pin is breached in order to allow the electrolyte to act on the composition. Said operation may conveniently be carried out by, for example, laser cutting. The

10 procedure is generally carried out by ensuring that the fuel pin is held in a suitable position and indexed in order to achieve even removal of cladding, and thereby minimise stressing of the cladding; this also ensures that the pin remains as straight as possible. The pin is then loaded into the electrorefining cell.

15 Thus, the first embodiment of the invention provides an electrorefining cell which generally comprises a central anode basket, an outer vessel, which is conveniently tubular in shape, and a cathode insulated from the lid and base of the vessel. Preferably the cathode comprises steel, and is cylindrical in shape; it should be non-adherent in order to facilitate removal of metals such as uranium from its surface.

20 The second embodiment of the invention differs from this design in that the fuel pin itself forms the anode. In any event, the cell is designed with provision for the application of an inert atmosphere, and for the removal of fission product off gases to a central off gas treatment system.

25 The application of a suitable potential difference between the anode and the cathode results in electrochemical oxidation of the metal at the anode, causing it to enter into the liquid electrolyte medium. The soluble metal species is then electro-transported to the cathode where a reduction process occurs, which results in the deposition of the metal at the cathode.

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Ideally, the electrorefiner should be designed to have significantly greater length than width, providing a long, thin device which facilitates efficient pumping of the electrolyte through the apparatus. Such a design also maximises the available surface area of the electrodes and is beneficial in delivering the criticality constraints

5   imposed on the system.

When the electrolyte comprises a molten salt, it may comprise any molten salt well known to those skilled in the art. Thus, for example, a LiCl/KCl molten salt eutectic mixture may be used in the process of the invention, for example a LiCl/KCl eutectic

10   melt comprising 41.5 mol.% KCl, with m.p. 361 °C. Preferably, however, the electrolyte comprises an ionic liquid, such as 1-ethyl-3-methylimidazolium chloride

Ionic liquids have advantages over conventional molten salts. As they operate at closer to ambient temperatures, they are probably less aggressive towards

15   construction components, and engineering and process costs are likely to be reduced. They also have advantages over organic solvents such as acetonitrile, in being non-volatile, with consequent environmental benefits. Furthermore, metal species are usually more soluble in ionic liquids than in organic solvents. In addition, ionic liquids offer the ability to selectively "fine tune" the electrochemical window of the

20   solvent in which the metal is dissolved, and from which purification or recovery is taking place.

Ionic liquids can be used to electrodeposit metals which are generally considered to be electropositive, for example, metals whose electrode reduction potentials are more

25   positive than the H_3O^+ ion. An ionic liquid can be used for this task if there are benefits of using ionic liquids over aqueous based solutions. An example is the electroplating industry (for instance silver) where there are safety and environmental benefits of using ionic liquids rather than cyanide ion solutions.

30   Preferably the cation component of the ionic liquid is an organic cation, for instance, a nitrogen heterocycle such as N-substituted pyridinium (preferably alkylpyridinium,

for instance, N-butylpyridinium), N,N'-disubstituted imidazolium (preferably N,N'-dialkylimidazolium, for instance, 1-ethyl-3-methylimidazolium), and substituted ammonium and phosphonium, for instance, tetraalkylammonium (for instance, tetraoctylammonium) or tetraalkylphosphonium (for instance,

5   tributyltetradecylphosphonium).

The substituents are preferably hydrocarbyl and more preferably alkyl, which may be branched. The hydrocarbyl (e.g. alkyl) groups usually contain from 1 to 18 carbon atoms and some usually from 1 to 8 carbon atoms.

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The cation may therefore preferably be a disubstituted imidazolium ion where the substituent groups take the form C_nH_{2n+1} for $1 \leq n \leq 8$, and the substituent groups are linear or branched groups. In preferred disubstituted imidazolium ions one substituent has n = 1, 2, 3 or 4 (of which methyl is particularly preferred) and the

15   other has n = 2, 3, 4, 5, 6, 7 or 8 (of which octyl, hexyl and more particularly butyl are preferred, linear groups being preferred). Alternatively, the cation might be a substituted tetraalkylammonium or tetraalkylphosphonium ion, where the alkyl groups take the form of C_nH_{2n+1} for $1 \leq n \leq 6$, and are linear or branched groups. Preferred examples include tetrabutylammonium and tetrabutylphosphonium.

20   However, the alkyl groups are preferably of different lengths resulting in asymmetrical substitution. Alternatively, the cation might be a substituted pyridinium ion, where the substituent group also takes the form C_nH_{2n+1} for $1 \leq n \leq 8$, and the substituent groups are linear or branched groups; suitable substituents include butyl, 2-(2-methyl)propyl, 2-butyl and octyl but straight chain alkyl, especially butyl,

25   is preferred.

The ionic liquid may be a mixture of two or more ionic liquids, which together provide the desired properties such as, for instance, a lower viscosity. An example is a mixture of disubstituted imidazolium in which the components of the mixture have

30   alkyl groups of different lengths, e.g. a mix of 1-octyl-3-methylimidazolium chloride ([emim]Cl) and 1-ethyl-3-methylimidazolium chloride ([omim]Cl).

The anion component is likely to be an inorganic species such as halide (for instance, chloride), nitrate, sulphate, tetrafluoroborate, hexafluorophosphate or tetrachloroaluminate, triflate which is trifluoromethanesulfonate ($CF_3SO_3^-$), and bistrifylimide which is bis(trifluoromethanesulfonyl)imide ($[CF_3SO_2)_2N]^-$).

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Preferably the ionic liquid will be pre-loaded with metal ions, in order that the electrorefining process can be initiated. Such pre-loading may be achieved by, for example, the addition to the ionic liquid of a soluble uranium salt or a salt such as cadmium chloride. Addition of a metal salt, such as cadmium chloride, results in the

10   reaction of this metal salt with uranium metal, creating metal ions in the solution.

Pre-loading with uranium ions may also be achieved by displacement of a metal chloride, such as AgCl or $CdCl_2$. Alternatively, pre-loading with uranium ions may be achieved by destructive reduction of the electrolyte. At the anode uranium is

15   oxidised to a soluble uranium species and, within a cathode compartment separated from the bulk of the solution, the organic cation of the ionic liquid or sacrificial organic reagent added to it, is destroyed.

In the case of electrolytes which comprise ionic liquids, the cell is operated at around

20    $100°C$ in order to ensure that the liquid is maintained above its melting point; a suitable heating medium is employed for this purpose.

The process of the invention can be applied to a variety of metal fuel feeds. Preferably the metal composition to be treated is irradiated nuclear fuel and the metal

25   to be separated is uranium. Uranium or a uranium compound, and possibly other transuranic metals or compounds, will be deposited at the cathode in a purified form. Any fission products and transuranics, including plutonium, which are oxidised from the anode together with the uranium, will remain in the electrolyte. After the uranium electrorefining operation has been carried out, the electrolyte is subjected to

30   further processing if plutonium removal is required.

By contrast with a process involving chemical dissolution, in an electrochemical process there can be much greater selectivity of the species to be dissolved. The potential at the anode can be controlled, such that metals which are more electropositive than uranium, and with larger negative Gibbs free energies associated

5   with the species formed in solution, are the only metals which dissolve at the anode. This is the first separation step, as many of the more noble metals will remain behind in an anodic sludge. The electrolyte now contains a solution of metal ions including uranium and those of more electropositive species. A suitable potential is applied at the cathode, whereby uranium and metals less electropositive than uranium are

10   electrodeposited. This should only include uranium, as those less electropositive metals have not been anodically dissolved. It is anticipated that the noble metals will not be rinsed from the anode basket during operation of the cell, due to the design of the basket.

15   The uranium deposited at the cathode is swept away from the surface of the electrode to the bottom of the vehicle, where it enters a solid/liquid separator, such as a hydrocyclone, where the uranium is removed from the bulk electrolyte stream. The stream of electrolyte is then returned to the top of the electrorefiner, whilst the uranium stream is sent to a further solid/liquid separator where the slurry is further

20   concentrated and the supernatant electrolyte is returned to the system.

The process of the present invention is analogous to the ANL process, wherein a metallic fuel feed is electrorefined and a uranium metal product is collected on a cathode. However, the process of the present invention shows significant advantages

25   over this prior art method in that it is a continuous process and is free from the moving components, such as rotating anodes, which often cause problems with the ANL process. The present process also allows for the use of ionic liquids, as well as molten salts, in its operation.

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DETAILED DESCRIPTION OF THE INVENTION

The invention will now be described in detail, though without limitation, by reference to the accompanying drawings, in which

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Figure 1 shows apparatus for performing a process according to a first embodiment of the present invention, and

Figure 2 shows apparatus for performing a process according to a second
10   embodiment of the present invention.

Referring firstly to Figure 1, there is provides an apparatus which comprises an electrorefining cell 1 comprising a central anode basket 2, an outer vessel 3 which is tubular in shape, and a cathode 4, insulated from the lid and base of the vessel. The
15   cathode is cylindrical in shape and preferably comprises stainless steel. A length of piping 5 leads from the electrorefining cell to a solid/liquid separator 6 which incorporates two outlets; from the first outlet issues the metal product stream A, whilst the second outlet is connected to a pump 7 which recycles the electrolyte to the top of the electrorefining cell 1, which also helps to facilitate the removal of dendritic
20   growth. The shredded metal composition, typically cropped sections of spent nuclear fuel 8, is loaded into the anode basket 2 and the electrolyte is introduced tangentially at the top of the cell 1 to immerse the anode basket, together with the cathode.

Turning now to Figure 2, there is shown an apparatus which comprises an
25   electrorefining cell 1 comprising a fuel pin 9 which serves as the anode, an outer vessel 3 which is tubular in shape, and a cathode 4, insulated from the lid and base of the vessel. The cathode is cylindrical in shape and preferably comprises stainless steel. A length of piping 5 leads from the electrorefining cell to a solid/liquid separator 6 which incorporates two outlets; from the first outlet issues the metal
30   product stream A, whilst the second outlet is connected to a pump 7 which recycles

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the electrolyte to the top of the electrorefining cell 1. The electrolyte is introduced tangentially at the top of the cell 1 to immerse the anode and cathode.

5　In either embodiment, the wall of the electrorefiner is separate from the cathode so as to allow the cathode to be electrically isolated from the rest of the vessel and, in addition, to allow for the provision of secondary containment in the event that the cathode wall should be breached in any way.

10　In each case, a suitable potential difference is then applied between the anode and cathode, such that the metal is electrochemically oxidised at the anode, and enters into the electrolyte medium. The soluble metal species is then electrotransported to the cathode, where a reduction process occurs. Contaminants with more positive reduction potentials than the metal in question remain unoxidised in the anode basket. Similarly, contaminants with more negative reduction potentials than the 15　metal remain unreduced in solution.

Electroreduction of the soluble metal species then results in the deposition of metal (or a metal compound) at the cathode. Provided that a suitable oxidising potential is applied at the anode and a suitable reduction potential is applied at the cathode, the 20　metal or a compound thereof will be deposited at the cathode in a purified form.

The process is particularly suited to the treatment of spent nuclear fuel, allowing for the recovery of uranium at the cathode. In such a process, the electrolyte will contain fission product compounds and compounds of the actinide elements which are 25　oxidised from the cathode with the uranium and it must be stripped of these contaminants before its subsequent re-use. This may be achieved by any one or a combination of a number of different routes, wherein these contaminants are separated from the electrolyte stream after passing through the pump 7 and removed as a stream B before the electrolyte is recycled to the top of the electrorefining cell 1. 30　Selected fission products and actinides such as plutonium can be electrochemically extracted through the application of a suitable potential using a liquid metal cathode

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such as a mercury electrode. Alternatively, dissolved plutonium may be co-deposited on a further cathode with uranium, irrespective of whether the metals are deposited in the metallic state (in the (0) oxidation state), as complexes or as oxides. Such co-deposition is useful in the manufacture of mixed oxide fuels.

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As the electrolyte recycles through the electrorefining cell 1, it sweeps the uranium deposited at the cathode away from the surface of the electrode to the bottom of the vehicle, where it is able to enter the solid/liquid separator 6, where the uranium is removed from the bulk electrolyte stream.

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If oxide fuels are to be treated there will probably be a need for a pre-treatment step, such as that performed in the ANL Lithium reduction process, to reduce the oxide fuel and form a metal feed. In the process according to the first embodiment of the invention, the metal fuel may also undergo a decladding process. This could take a

15 number of forms such as mechanical removal or chemical dissolution of the cladding.

Selective deposition of a metal from a solution containing its ions is well known in the art and does not require detailed explanation here. However all metal ions in a solution will have different electrode reduction potentials to reduce the ions to a

20 lower positive valency, or to reduce them to zero valency. Electrode reduction potentials are dependent upon the element, the oxidation state of the ion in the solvent and to the presence of other ions or molecules. If a potential is applied across a solution then all metal ions with a more positive potential will be deposited on the cathode. Metal ions with a more negative potential will remain in solution. Once a

25 particular ion has been removed from the solution, the electrode can be removed and replaced with a new one, biased at a slightly more negative potential, for the deposition of the next metal with a more negative reduction potential. If it is desired to deposit two metals together, then a potential more negative than the reduction potential for both ions is applied.

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Fission products may alternatively or additionally be removed from the electrolyte by the addition of an organic solvent. Addition of an organic species results in the precipitation of fission product compounds. The precipitate can be filtered from the electrolyte and calcined to convert to oxide prior to a vitrification step. Cleaned

5   electrolyte can then be recycled to the electrorefiner.

CLAIMS

1.   An electrorefining process for separating a metal from a composition including the said metal, the method comprising forming an electrorefining

5   cell having an anode, a cathode and an electrolyte, wherein the anode comprises the metal and the electrolyte comprises a substance which is liquid at its operating temperature and at this temperature is comprised wholly or largely of ionic species, and applying a sufficient potential difference between the anode and the cathode to cause the metal to transfer from the anode to the

10   cathode and to be deposited thereon, wherein the gap between the anode and the cathode is minimised, the electrolyte is circulated at high velocity through the cell, and the available surface area of the cathode is maximised by providing the metal in a form which has a large surface area per unit volume.

15   2.   An electrorefining process as claimed in claim 1 wherein the inter-electrode gap between the anode and the cathode is in the range of from 1 mm to 30 mm.

3.   An electrorefining process as claimed in claim 1 or 2 wherein the electrolyte

20   velocity is in the range from 0.6 m/sec to 25 m/sec.

4.   An electrorefining process as claimed in any one of claims 1, 2 or 3 wherein the fluid flow and electrolyte parameter combination leads to a Reynolds Number of greater than 2000.

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5.   An electrorefining process as clamed in claim 4 wherein the Reynolds Number is in the region of 3000.

6.   An electrorefining process as claimed in any one of claims 1 to 5 wherein the

30   composition including the metal comprises spent nuclear fuel.

7.   An electrorefining process as claimed in any one of claims 1 to 6 wherein the anode is in the form of a basket, and the metal composition is provided in a divided form within the said basket.

5   8.   An electrorefining process as claimed in any one of claims 1 to 6 wherein the metal composition is provided in the form of a long, thin rod which itself forms the anode.

9.   An electrorefining process as claimed in claim 7 wherein the metal

10   composition comprises an assembly of fuel pins which are dismantled to single pins, cropped into small sections by means of a single pin cropping machine and then loaded into the anode basket.

10.   An electrorefining process as claimed in claim 8 wherein the metal

15   composition comprises an assembly of fuel pins which are dismantled to single pins, a single fuel pin then acting as the anode.

11.   An electrorefining process as claimed in claim 7 wherein the electrorefining cell comprises a central anode basket, an outer vessel which is tubular in

20   shape, and a cylindrical cathode insulated from the lid and base of the vessel, said cathode comprising steel.

12.   An electrorefining process as claimed in claim 8 wherein the electrorefining cell comprises an anode comprising a fuel pin, an outer vessel which is

25   tubular in shape, and a cylindrical cathode insulated from the lid and base of the vessel, said cathode comprising steel.

13.   An electrorefining process as claimed in claim 10 or 11 wherein the electrorefining cell additionally comprises a solid-liquid separator.

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14.   An electrorefining process as claimed in claim 13 wherein said solid/liquid separator comprises a hydrocyclone.

15.   An electrorefining process as claimed in any preceding claim wherein the substance which is liquid at its operating temperature and at this temperature is comprised wholly or largely of ionic species comprises a molten salt.

16.   An electrorefining process as claimed in claim 15 wherein the molten salt comprises a LiCl/KCl molten salt eutectic mixture.

17.   An electrorefining process as claimed in any of claims 1 to 14 wherein the substance which is liquid at its operating temperature and at this temperature is comprised wholly or largely of ionic species comprises an ionic liquid.

18.   An electrorefining process as claimed in claim 17 wherein the cation component of the ionic liquid is an organic cation.

19.   An electrorefining process as claimed in claim 18 wherein the organic cation is   N-substituted   pyridinium,   N,N'-disubstituted   imidazolium, tetraalkylammonium or tetraalkylphosphonium.

20.   An electrorefining process as claimed in claim 19 wherein the organic cation includes alkyl groups which are linear or branched and not all of the same chain length.

21.   An electrorefining process as claimed in any one of claims 17 to 20 wherein the anion component is halide, nitrate, sulphate, tetrafluoroborate, hexafluorophosphate or tetrachloroaluminate.

22. An electrorefining process as claimed in any one of claims 17 to 20 wherein the anion component is trifluoromethanesulfonate bis(trifluoromethane sulfonyl)imide.

5 23. An electrorefining process as claimed in any of claims 17 to 22 wherein the ionic liquid is pre-loaded with metal ions.

24. An electrorefining process as claimed in claim 23 wherein the ionic liquid is pre-loaded with metal ions by the addition of a soluble uranium salt.

10

25. An electrorefining process as claimed in claim 23 wherein the ionic liquid is pre-loaded with uranium ions by displacement of a metal chloride.

26. An electrorefining process as claimed in claim 25 wherein the metal chloride
15 is AgCl or CdCl$_2$.

27. An electrorefining process as claimed in claim 23 wherein the ionic liquid is pre-loaded with uranium ions by destructive reduction of the electrolyte.

20 28. An electrorefining process as claimed in any one of claims 17 to 27 wherein, after use in the process, the ionic liquid is purified for further use.

29. An electrorefining process as claimed in any preceding claim wherein purified metal is deposited at the cathode.

25

30. An electrorefining process as claimed in any preceding claim wherein the metal is deposited at the cathode as a compound.

31. An electrorefining process as claimed in any preceding claim wherein the
30 metal to be separated is uranium and/or plutonium.

32.   A process for the reprocessing of spent nuclear fuel, the process including a process of any preceding claim.

5
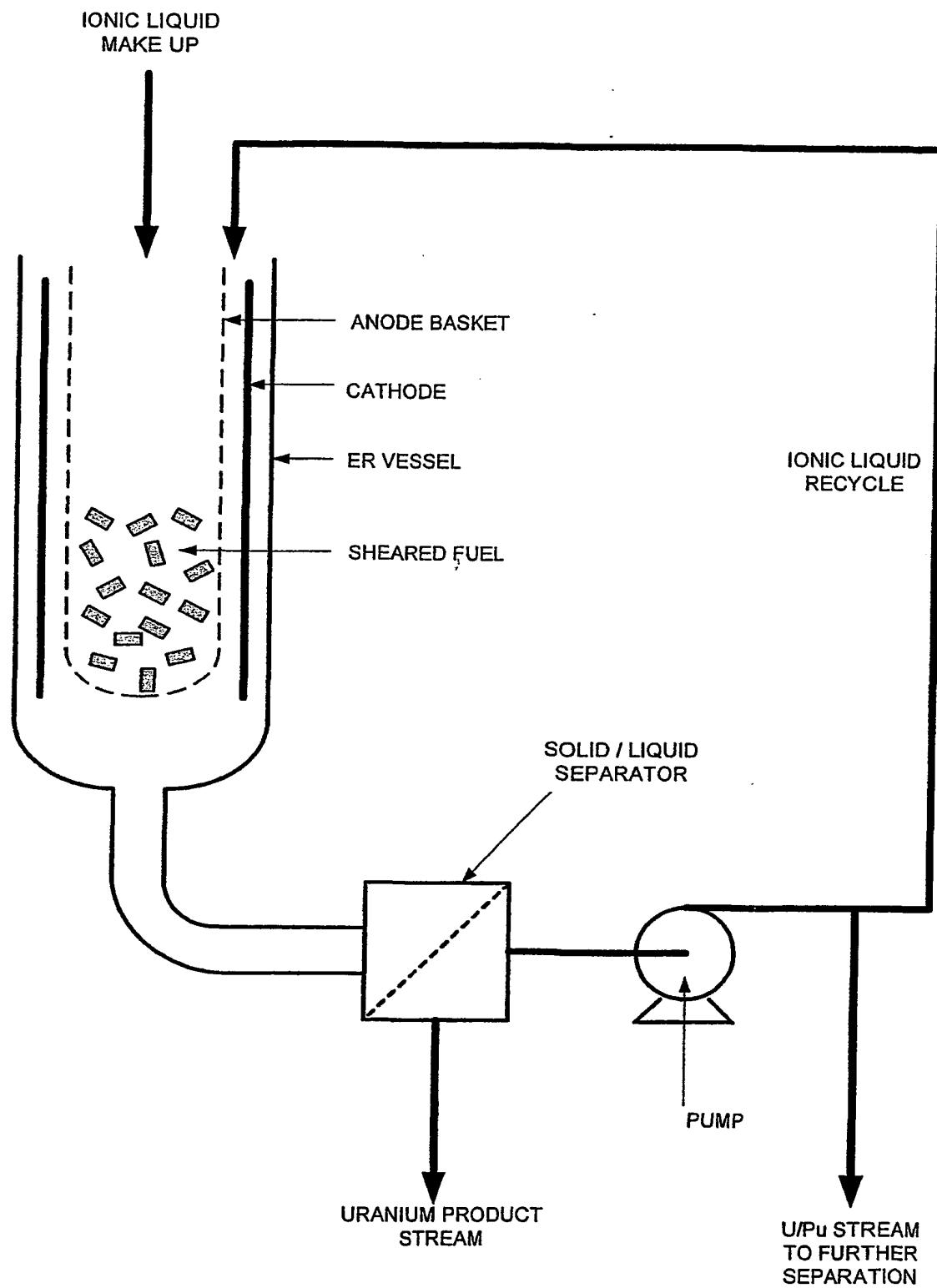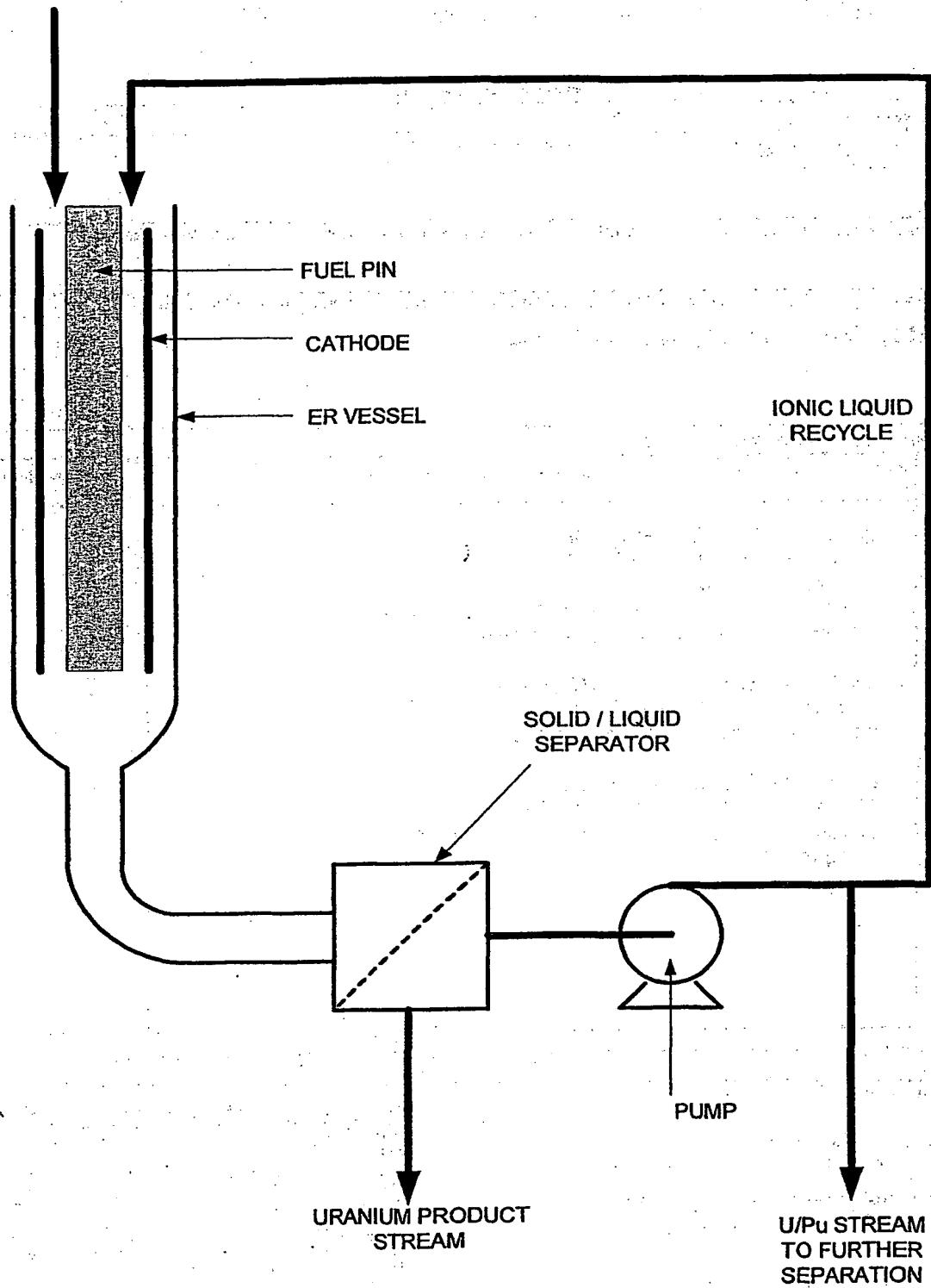
IONIC LIQUID
MAKE UP

ANODE BASKET

CATHODE

ER VESSEL

IONIC LIQUID
RECYCLE

SHEARED FUEL

SOLID / LIQUID
SEPARATOR

PUMP

URANIUM PRODUCT
STREAM

U/Pu STREAM
TO FURTHER
SEPARATION

FIGURE 1

1/2

IONIC LIQUID
MAKE UP

FUEL PIN

CATHODE

ER VESSEL

IONIC LIQUID
RECYCLE

SOLID / LIQUID
SEPARATOR

PUMP

URANIUM PRODUCT
STREAM

U/Pu STREAM
TO FURTHER
SEPARATION

FIGURE 2

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7   C25C7/00   C25C3/34   G21C19/48

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7   C25C   G21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 650 053 A (E. C. GAY) 22 July 1997 (1997-07-22) column 2, line 13 – line 17 column 5, line 43 – line 47 column 6 –column 8; claims 1-14	1
A	US 5 531 868 A (W. E. MILLER) 2 July 1996 (1996-07-02) column 5 –column 8; claims 1-19	1
A	US 5 380 406 A (J. A. HORTON) 10 January 1995 (1995-01-10) column 3, line 25 –column 5, line 26 figure 1	1

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X	Further documents are listed in the continuation of box C.		X	Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the International filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27 June 2002	04/07/2002

Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Authorized officer Groseiller, P

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
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International Application No

PCT/GB 02/00729

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			EP	1212756 A1	12-06-2002
			WO	0113379 A1	22-02-2001

BDOCID: <WO_____02066712A1_I_>